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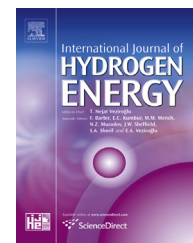
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Tri-reforming of methane over Ni@SiO₂ catalyst



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ABSTRACT

A nickel-silica core@shell catalyst was applied for a methane tri-reforming process in a fixed-bed reactor. To determine the optimal condition of the tri-reforming process for production of syngas appropriate for methanol synthesis the effect of reaction temperature (550–750 °C), CH₄:H₂O molar ratio (1:0–3.0) and CH₄:O₂ molar ratio (1:0–0.5) in the feedstock was investigated. CH₄ conversion rate and H₂/CO ratio in the produced syngas were influenced by the feedstock composition. Increasing the amount of steam above the proportion of CH₄:H₂O 1:0.5 reduced the H₂:CO molar ratio in produced syngas to ~1.5. Increasing oxygen partial pressure improved methane conversion to 90% at 750 °C. At low ~550 °C reaction temperature the tri-reforming process was not effective with low hydrogen production (H₂ yield ~20%) and very low <5% CO₂ conversion. Increasing reaction temperature increased hydrogen yield to ~85% at 750 °C. From all the tested reaction conditions the optimal for tri-reforming over the 11%Ni@SiO₂ catalyst was: feed composition with molar ratio CH₄:CO₂:H₂O:O₂:He 1:0.5:0.5:0.1:0.4 at T = 750 °C. The results were explained in the context of characterisation of the catalysts used. The obtained results showed that the tri-reforming process can be applied for production of syngas with composition suitable for methanol synthesis.

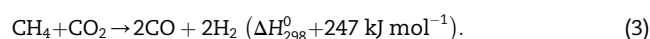
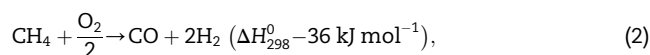
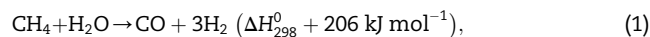
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Introduction

Methane reforming is a well established industrial process for syngas production. The goal of methane reforming is to achieve high methane conversion with the required H₂:CO ratio without coke deposition. The process can sometimes be combined with CO₂ conversion and utilisation. However, that process requires high energy input and there is a risk of coke deposition that would deactivate the catalyst [1].

In the novel process of tri-reforming, syngas production and CH₄ conversion is possible without CO₂ separation and with relatively low energy consumption [2]. The fact that it is not necessary to separate CO₂ from methane can reduce the

cost of reforming and at the same time can reduce the volume of CO₂ emissions. The tri-reforming process combines the three generally used methane reforming processes into one. In the tri-reforming of methane in a single reactor, the following reactions are coupled: methane steam reforming (1), methane partial oxidation (2) and carbon dioxide reforming of methane (3):



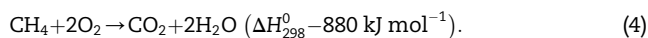
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The highly exothermic complete methane oxidation (4) can also occur, which increases energy efficiency:



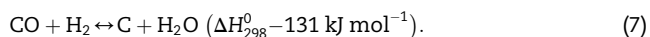
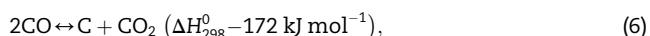
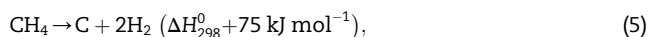
In line with this, the process combines the endothermic reactions of steam (1) and dry (3) reforming with exothermic partial (2) and complete oxidation of methane (4). Addition of oxygen to the reactor can generate heat required by steam and dry reforming of methane and make the reforming process more energy efficient [3]. Halmann and Steinfeld proposed to combine the tri-reforming process with a lime carbonation [4] or with a carbothermic reduction of iron [5] to achieve the fully thermo-neutral process.

In the tri-reforming process, CO_2 is utilized in the methane dry reforming reaction (3). Moreover, flue gas from the combustion processes of power plants can be used as a CO_2 source for tri-reforming [2]. An average flue gas composition contains CO_2 3–16%, O_2 2–13%, H_2O 6–8%, N_2 75–76% [6].

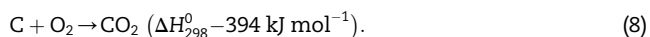
The tri-reforming process is more energy efficient than steam reforming or dry reforming of methane for production of syngas with H_2 :CO molar ratio in the range of 1.5–2, as required by methanol synthesis [5]. Adjusting the molar ratio of compounds during tri-reforming allows control of the H_2 :CO ratio in the produced gases to the required level.

The tri-reforming process can be used for transformation of low quality, CO_2 -rich natural gas into useful syngas. Tri-reforming is also a good option for hydrogen production from biogas [7]. In biogas, the molar ratio of CH_4 : CO_2 is usually sufficient for tri-reforming. Furthermore, the tri-reforming process can be used to obtain syngas by upgrading gas from biomass gasification.

During the reforming process of methane, coke formation sometimes occurs during methane cracking (5), the Boudouard reaction (6) and reduction of CO to carbon (7):



Applying tri-reforming for reforming of methane can reduce the coke formation problem. During the tri-reforming process coke formation may occur simultaneously with the reduction of formed coke due to the coke oxidation (reaction 8 and reverse of reaction 7)



Reaction (5) tends to generate carbon at higher (~750 °C) reaction temperature. The thermodynamic equilibrium of reactions (6) and (7) can be shifted to the right side at low (~550 °C) reaction temperature. At higher reaction temperature reactions (6) and (7) can be influenced by equilibrium limitations.

So far, the concept of methane tri-reforming has been studied at a laboratory scale and mathematical models of tri-reforming reactors have been analysed. Minutillo and Perna [6,8] using thermal efficiency calculations suggested optimal

operating conditions for tri-reforming of 850 °C and a molar ratio between flue gas and methane of 2–3.

The most popular catalysts for tri-reforming of methane are nickel supported by a wide range of different materials (Al_2O_3 , ZrO_2 , CeO_2 etc), similar to steam or to dry reforming. In tri-reforming of methane, there is a risk of re-oxidation of catalyst by oxygen present in the feed. For catalysts resistant to coke formation, re-oxidation can be the main reason of catalyst deactivation [9]. In line with this, not all catalysts applicable for methane steam reforming can be used for tri-reforming. Solov'ev et al. [3] observed that $\text{NiO}/\text{Al}_2\text{O}_3$ catalyst which had almost 100% of methane conversion during steam reforming, gave a methane conversion of only 15% during tri-reforming.

The mixture of gases produced by the tri-reforming process contains mostly H_2 and CO and can be applied for solid oxide fuel cells (SOFC) and molten carbonate fuel cells (MCFC) for electricity generation [10,11]. The syngas produced during the tri-reforming process usually has a H_2 :CO ratio of 1.5–2 [12]. That proportion makes produced syngas suitable for use in the Fischer–Tropsch process [13], for methanol synthesis [8] or for dimethyl-ether synthesis [14,15].

A variety of compositions of synthesis-gas can be used for the Fischer–Tropsch process. The required H_2 /CO ratio is usually around 1.7–2.15 depending on the catalyst used and operating conditions [16,17]. The maximum output of methanol can sometimes be obtained for the H_2 /CO ratio 2.5 [18]. The ideal required H_2 /CO ratio for synthesizing methanol is 2. However, the reaction conditions and especially the addition of CO_2 can change the required ratio [19,20].

Silica is rarely used as a catalyst support in steam reforming because as the steam pressure is increased silica can become volatile. That would damage the support structure and reduce the surface area of a catalyst prepared by a wet impregnation method. The tested Ni@SiO_2 catalyst had the core@shell structure. In that structure the silica core is completely covered by a nickel shell and that should limit access to the silica surface. In addition, the reduced water partial pressure in the tri-reforming process can decrease the eventual carryover of silica in the form of vapour species. The core@shell structure of the catalyst had the advantage of high utilisation of metal and enhancement of catalyst activity. No significant change to the catalyst structure was observed after 4 h reaction. An alternative solution for the eventual silica vaporisation is to dissolve silica cores by alkaline solution to obtain nickel hollow nanospheres [23].

The aim of this work was to establish the optimum conditions for the tri-reforming process with a nickel–silica core@shell catalyst. The variables studied were chosen according to literature data and according to limitations of the setup used. The Ni@SiO_2 core shell catalyst was selected due to its satisfactory results in methane steam reforming reactions [21]. No reports have been found on characterisation of SiO_2 supported catalyst for methane and CO_2 conversion in the presence of O_2 and H_2O . In addition, the application of core shell catalysts has not yet been studied for tri-reforming processes. However, some authors [22] tested catalyst prepared by a deposition-precipitation method. In this paper, an evaluation was made of the ability to control the H_2 :CO ratio in produced syngas by adjusting the molar ratio of compounds in

feedstock to obtain synthesis-gas suitable for methanol synthesis.

Experimental

Catalyst preparation and characterisation

The catalyst was prepared according to the method described previously [21]. Silica spheres were prepared by the Stöber process and were covered by nickel using the deposition-precipitation method [23]. The Stöber process combined with the deposition-precipitation of Ni allows reproductive formulation of particles with required size. Silica spheres were covered by three-dimensional Ni film. Core shell structured catalysts, especially those with a thin shell, exhibit enhanced catalytic properties. After drying in air at 105 °C overnight, the prepared catalyst was calcined at 700 °C for 4 h in air, at a heating rate of 5 °C min⁻¹. Characterisation of freshly prepared catalyst was described previously [21]. It was confirmed that the catalyst had a core@shell structure with silica cores covered by Ni shells [21]. The coated catalyst had a nickel concentration of ~11 wt% (11%Ni@SiO₂). The particle size measured from SEM micrographs was in the range of 0.7–1.0 µm with an average diameter of ~0.9 µm for both the fresh and the spent catalyst. The surface area of the catalyst after calcination was ~68.1 m² g⁻¹.

The properties of the spent catalyst were analysed using the same procedures as for the freshly prepared catalyst [21] for better understanding of catalyst activity in the tri-reforming process. The BET surface area, average pore diameter and total pore volume were determined by N₂ adsorption. The crystallization behaviour of the catalyst was analysed by X-ray powder diffraction (XRD). The surface chemistry of the catalysts were analysed using Fourier transform infrared spectroscopy (IR). The morphological properties of the tested catalyst were measured using a scanning electron microscope. The coke deposition was analysed using temperature-dependent mass change profiles (TGA). Samples of spent catalyst were examined by a temperature programmed oxidation method (TGA-TPO) by heating samples of the used catalyst (10–20 mg) in air at a flow rate of 50 ml min⁻¹ over the temperature range 25–900 °C at a rate of 10 °C/min. Sample preparation techniques and details of equipment used were described previously [21].

Catalytic reaction

The performance of the 11%Ni@SiO₂ catalyst for tri-reforming of methane was tested in a bench scale, continuous flow, fixed-bed reactor. The stainless steel reactor with inner diameter 5 mm operated at atmospheric pressure was equipped with a gas flow control system and an on-line gas chromatograph (GC). For each test, 0.2 g of the catalyst (as a powder) was diluted with inert CSi (1:9). The catalyst was diluted to avoid gas pressure drop, particles clogging and catalyst bypassing. The reactor was installed into a tubular, electrically heated furnace. Prior to reaction, the catalyst was activated “in situ” at 650 °C with hydrogen flow 10 ml min⁻¹ during 1 h. After the reduction process, the reactor was purged

by nitrogen (100 ml min⁻¹, 5 min) then a gas mixture of CH₄:CO₂:O₂ and He (carrier gas) was switched into the reactor. The catalyst was tested under a constant flow rate of CH₄ 25 ml min⁻¹ at a temperature range of 550–750 °C. Steam was generated from deionised water fed to a heater (120 °C) by a pump at a flow of 0–0.06 ml min⁻¹ and mixed with the gas mixture directly before the reactor inlet. Helium was used as a carrier gas and as a balance in order to obtain the total gas flow constant. However, the flow rate of the feed varied accordingly to the amount of added steam for those experiments where the influence of steam partial pressure was investigated (Table 1). The effluent was cooled by passing through an ice trap where eventual liquid products were condensed. The on-line GC was used for quantitative and qualitative analysis of reaction products. CH₄ and CO₂ conversions were calculated from the molar concentrations of CH₄ and CO₂ respectively at the reactor inlet and outlet. For the CO₂ it was a net conversion that included eventual CO₂ generation from reactions (4), (6) and (8) and water-gas shift reaction.

The results of tri-reforming obtained with the 11%Ni@SiO₂ catalyst were compared with commercial catalyst HiFUEL™ R110 from Alfa Aesar at the reaction condition optimal for the 11%Ni@SiO₂ catalyst.

Results and discussion

Fig. 1 presents results of catalyst activity experiments as a function of reaction temperature. All reactions were carried out separately for each tested reaction temperature. No significant deactivation of the tested catalyst was detected in any of reactions during the first 4 h. Conversion of methane and conversion of CO₂ increased with increasing reaction temperature. Additionally, the H₂:CO molar ratio in produced syngas decreased at elevated reaction temperature. Increasing reaction temperature from 550 to 750 °C resulted in increasing methane conversion from 24% to above 70%. Over the same range of temperatures CO₂ conversion increased more than 10 times from 4% to 52%. Simultaneously, the H₂:CO molar ratio reduced from 3.7 to 2.6.

Increasing reaction temperature favoured endothermic reactions like steam (1) and dry (3) reforming of methane. This is particularly the case for dry reforming, as the highly endothermic reaction became more intensive at elevated temperature. As a result, with increasing reaction temperature methane and CO₂ conversion increased and enhanced CO

Table 1 – Effect of molar ratio between CH₄ and steam in the feedstock on tri-reforming performance.

Feed composition CH ₄ :CO ₂ :H ₂ O:O ₂ :He	Conversion [%]		H ₂ :CO molar ratio	Coke ^a [mg g _{cat} ⁻¹]
	CH ₄	CO ₂		
1:0.5:0.0:0.1:0.4	31.8	91.1	2.0	57 (±6.7)
1:0.5:0.5:0.1:0.4	73.0	55.6	2.6	5 (±1.6)
1:0.5:1.0:0.1:0.4	71.2	63.0	1.5	118 (±6.0)
1:0.5:3.0:0.1:0.4	73.1	42.8	1.7	112 (±2.0)

Average of results from 4 h methane tri-reforming over the 0.2 g of the 11%Ni@SiO₂ catalyst, T = 750 °C, CH₄ 25 ml min⁻¹.

^a Deposition after 4 h reaction.

production was observed. Moreover, the reverse water-gas shift reaction was thermodynamically favoured at high reaction temperature. The reverse water-gas shift reaction consumed part of the hydrogen produced by methane reforming and produced more CO. It was concluded that all added H₂O was converted at elevated reaction temperature. There were no liquid products after all reactions with the molar ratio of CH₄:H₂O 1:0.5 in the feedstock. The residual oxygen and water concentrations were essentially zero.

The tri-reforming process at the lowest reaction temperature of 550 °C was not effective, with only just above 20% methane conversion (Fig. 2). Conversion of CO₂ was significantly lower than of methane at that temperature. In the tri-reforming process, CO₂ is not only the reaction substrate but also the reaction product. During the reaction at 550 °C, the average CO₂ conversion was below 5%. Steam reforming (1) slowed down and dry reforming (3) probably terminated. Zhou et al. [24] suggested that dry reforming does not proceed at the temperature of the tri-reforming process below 650 °C. CO₂ conversion at 550 °C slightly decreased with reaction time, probably due to the carbon deposition (Fig. 2). At lower reaction temperature, the thermodynamic equilibrium favoured the forward direction of the water-gas shift reaction resulting in conversion of CO and steam to CO₂ and H₂, with an accompanying increase of CO₂ and H₂ concentration in produced syngas. Moreover, for a period of time, the phenomenon of negative CO₂ conversion was observed for the reaction at 550 °C (Fig. 2). CO₂ could be produced also by the complete (exhaustive) methane oxidation (4) at that reaction temperature. CO production was reduced at low reaction temperature, as it was thought that excess of added water reacted with CO in the water-gas shift reaction under these conditions.

Fig. 3 presents results of methane tri-reforming under different proportions of oxygen to methane in the feedstock, during the constant CO₂ and steam partial pressure in the feed. To obtain constant feed flow rate and constant CO₂ and steam partial pressure with increasing O₂ partial pressure accordingly decreased partial pressure of He used as a balance. All reactions were carried out separately for 4 h at each

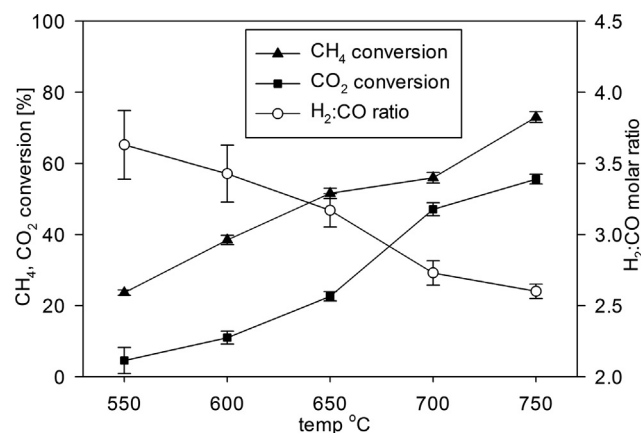


Fig. 1 – Effect of reaction temperature on CH₄ and CO₂ conversion and on the H₂:CO molar ratio – average of results from 4 h reaction. The molar ratio of feedstock CH₄:CO₂:H₂O:O₂:He was respectively 1:0.5:0.5:0.1:0.4, CH₄ 25 ml min⁻¹ over 0.2 g of the Ni@SiO₂ catalyst.

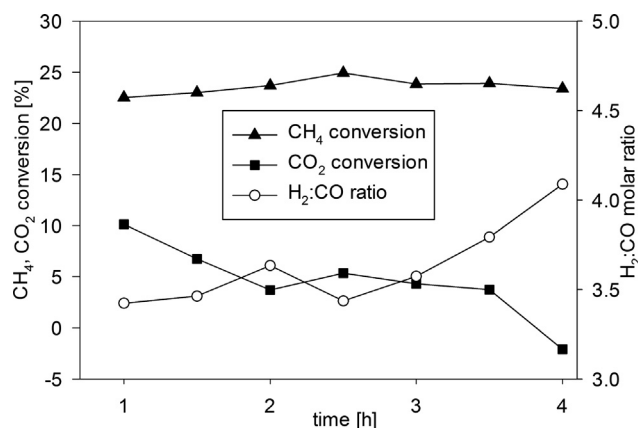


Fig. 2 – Catalytic activity of the Ni@SiO₂ catalyst at 550 °C. The molar ratio of feedstock CH₄:CO₂:H₂O:O₂:He was respectively 1:0.5:0.5:0.1:0.4, CH₄ 25 ml min⁻¹ over 0.2 g of the Ni@SiO₂ catalyst.

condition with no significant deactivation of the catalyst. It was observed (Fig. 3) that syngas with slightly different H₂:CO molar ratio was obtained by varying the O₂ partial pressure. Increasing the amount of oxygen added to the tri-reforming process improved methane conversion from 70% to 90%. However, hydrogen yield remained almost unchanged. Conversion of CO₂ decreased from 80% when no oxygen was added to reactor to ~55% for reactions with added oxygen.

Increased O₂ partial pressure promotes partial (2) and complete (4) oxidation of methane and that could result in high methane consumption without hydrogen production. As a result, there was less methane available for dry (3) and steam (1) reforming. Addition of O₂ resulted in methane oxidation (4) and CO₂ production which in turn affected the net CO₂ conversion. CO₂ conversion could be also affected by the coke oxidation reaction (8). Oxygen reacts quickly and was assumed to have been completely consumed in the tested temperature range, since there was no oxygen measured in produced gas for

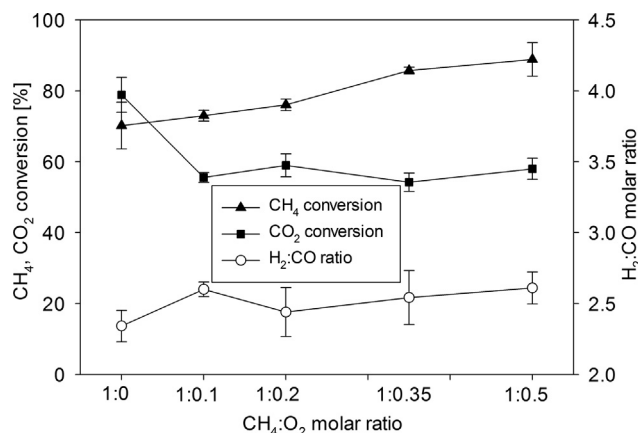


Fig. 3 – Effect of the inlet CH₄:O₂ molar ratio on CH₄ and CO₂ conversion and on the H₂:CO molar ratio – average of results from 4 h reaction. The molar ratio of the feedstock CH₄:CO₂:H₂O:O₂:He was respectively 1:0.5:0.5:0–0.5:0–0.5, CH₄ 25 ml min⁻¹ over 0.2 g of the Ni@SiO₂ catalyst, T = 750 °C.

the all tested reaction conditions. Walker et al. [22] suggested that the effect of rapid oxygen consumption occurs as a result of high affinity of O_2 for the catalyst active sites.

The influence of added O_2 on CO_2 conversion is not clear. Solov'ev et al. [3] observed that the influence of oxygen concentration is related to the catalyst structure. They noticed that addition of oxygen with the NiO/Al_2O_3 catalyst significantly reduced methane reforming, but for $NiO/Al_2O_3-La_2O_3$ or $NiO/Al_2O_3-CeO_2$ increased methane conversion and the $H_2:CO$ ratio, but reduced conversion of CO_2 .

It can be concluded that CH_4 conversion increased with increasing reaction temperature and with increasing oxygen concentration. In line with this observation, as the amount of added oxygen increased, the required reaction temperature to obtain high CH_4 conversion became lower. Moreover, the positive aspect of oxygen addition was to enhance catalyst activity by oxidation of deposited carbon (8).

With increasing the amount of steam added to the process from molar ratio of $CH_4:H_2O = 0$ to 0.5 the CH_4 conversion increased from ~30–73% and conversion of CO_2 decreased accordingly from 91 to 56% (Table 1). It can be concluded that in the situation where no water was added to the reaction (auto-thermal reforming) there was no competition for CO_2 to access to catalyst active sites. That resulted in intensive CO_2 conversion, above 90% and relatively small (~30%) CH_4 conversion. The ratio between H_2 and CO in the produced syngas was around 2. That was higher than the stoichiometric value obtained from only the dry reforming reaction (3). The additional hydrogen could be deduced to have come from methane partial oxidation and methane cracking reaction (5). The activity of the methane cracking reaction (5) could also explain the higher coke deposition. It must be pointed out that for the feed composition of $CH_4:CO_2:H_2O:O_2:He$ 1:0.5:0:0.1:0.4, where no H_2O was added, there was not sufficient substrates for complete methane reforming thus the observed lower CH_4 conversion was expected.

The presence of steam promoted the methane steam reforming reaction (1). That led to higher concentration of H_2 in the produced syngas and higher (2.6) $H_2:CO$ molar ratio. The fact that the $H_2:CO$ ratio was still below 3 was probably due to the reverse water-gas shift reaction which consumed some of the produced H_2 . According to the literature [22] it is possible that water competes with CO_2 for active sites upon the catalyst and that resulted in reduction in CO_2 conversion. Reaction of CH_4 with steam (1) is thermodynamically favoured over the reaction with CO_2 (3). The coke deposition was very small, only 5 $mg\ g_{cat}^{-1}$.

Methane conversion changed only slightly with further increase in the water partial pressure. The proportion between H_2 and CO in the produced syngas decreased to around ~1.5, the value required for methanol synthesis. However, the amount of deposited coke increased significantly (Table 1). The decrease in $H_2:CO$ molar ratio was probably due to the reverse water-gas shift reaction. The influence of steam on coke deposition is still not clear. Excessive water was collected by the ice trap where the amount of steam added to reaction was above the ratio $CH_4:H_2O$ 1:0.5. The volume of redundant water increased with increasing water partial pressure in the feedstock.

Table 2 presents analyses of the spent catalyst after exposure to different reaction conditions. It can be seen that both the reaction temperature and the amount of oxygen added to the reactor influenced the catalyst condition. Increasing reaction temperature from 550 to 750 °C reduced the amount of deposited coke from 99 to 5 $mg\ g_{cat}^{-1}$. The higher coke deposits in the reactions at 550 and 650 °C were thought to be due to the fact that at lower reaction temperature, exothermic reactions were favoured. At temperature 550–650 °C the thermodynamic equilibrium favoured the Boudouard reaction (6) and CO reduction reaction (7) which could result in high coke deposition.

Increasing oxygen concentration from 0 to 0.2 M fraction decreased the coke deposition at constant reaction temperature of 750 °C (Table 2). Addition of oxygen in the proportion $CH_4:O_2$ 0.1 was sufficient to reduce the coke deposition to 5 $mg\ g_{cat}^{-1}$ from 24 $mg\ g_{cat}^{-1}$ without oxygen, although further increase in oxygen partial pressure did not further influence the coke deposit. It was thought that the effect of deposited coke reduction in the presence of oxygen was due to the carbon oxidation reaction (8). Moreover, higher oxygen concentration could increase temperature in the reactor by promoting oxidation and partial oxidation of methane. Higher temperature could shift thermodynamic equilibrium to the reverse Boudouard reaction (reverse of reaction (6)) and to reduction of coke deposition due to the presence of steam (reverse of reaction (7)). Furthermore, the reaction of oxygen with methane reduced the amount of methane available for eventual methane cracking reaction (5).

Referring to Table 2, the surface area of the catalyst changed after reaction if the tri-reforming process was carried out at temperature above 650 °C. The surface area decreased from 68.1 $m^2\ g^{-1}$ for the fresh catalyst to ~41 $m^2\ g^{-1}$ after reaction at 650 °C and to ~26.1 $m^2\ g^{-1}$ after reaction at 750 °C. Reduction in catalyst surface decreased with higher oxygen concentration in the feed. As the surface area of used catalyst decreased the average pore diameter increased. The decrease in the surface area of the catalyst could be due to the sintering of Ni particles, coke deposition or due to the formation of the clusters made of 2–3 catalyst particles. The eventual re-oxidation of Ni also could affect the catalyst surface area. The TGA analyses of spent catalyst showed that the coke formed during the tri-reforming process was oxidized at temperature 585–620 °C and that may suggest that the coke was in the graphite carbon form [25].

Table 2 – Effect of reaction temperature and the molar ratio between $CH_4:O_2$ in the feedstock on coke deposition.

Feed composition $CH_4:CO_2:H_2O:O_2:He$	Reaction temp.	BET surface area $[m^2\ g^{-1}]$	Coke deposition $[mg\ g_{cat}^{-1}]$
1:0.5:0.5:0.1:0.4	550 °C	59.6	99 (± 12.1)
1:0.5:0.5:0.1:0.4	650 °C	41.2	49 (± 11.0)
1:0.5:0.5:0.1:0.4	750 °C	26.1	5 (± 1.6)
1:0.5:0.5:0.2:0.3	750 °C	21.4	5 (± 1.0)
1:0.5:0.5:0.0:0.5	750 °C	34.7	24 (± 7.3)

The surface area of the fresh unused catalyst after calcination was ~68.1 $m^2\ g^{-1}$.

SEM scans of the catalyst after 4 h reaction were taken to analyse the catalyst morphology (Figs. 4 and 5). The particles of the spent catalyst looked similar to particles of the fresh catalyst described previously [21]. Cracks or breaks in nickel coating were not apparent on catalyst grain structure. SEM micrographs of the catalyst after the tri-reforming process confirmed formation of coke on catalyst surface during the reaction at low temperature. SEM analyses of the catalyst after the reaction at 550 °C showed some whisker structures believed to be carbon in the form of whisker carbon or nano-tubes (Fig. 4). The number of carbon tubes after the reaction at 750 °C was insignificant (Fig. 5), consistent with TPO analyses (Table 2). The number of clusters made of 2–3 particles was slightly higher after the reaction at 750 °C than that at 550 °C.

Fig. 6 presents results of FTIR analyses of the fresh and the spent catalyst. The characterisation of the freshly prepared catalyst was described previously [21]. The structure of the catalyst did not change significantly after the tri-reforming process. All the bands characteristic for the core@shell nickel–silica catalyst were detected for samples of the spent catalyst after all tested reaction conditions. Bands specific for nickel phyllosilicate (3649 , 3629 , 711 and 670 cm^{-1}) became less intensive after tri-reforming, probably due to Ni sintering and due to the higher (750 °C) reaction temperature. The catalyst was reduced at 650 °C and 2:1 nickel phyllosilicate can decompose at higher than 650 °C temperature [26].

The only difference between the fresh and the spent catalyst was the presence of several small new bands in the region of 1400 – 1600 and 2825 – 2890 cm^{-1} for the catalyst after reaction. The two minor bands at 2825 and 2890 cm^{-1} could be related to the symmetric and asymmetric stretching vibration of the C–H bonds associated to methylene groups connected to the aromatic rings or aliphatic groups [27]. After the tri-reforming process the “water” band at 1628 cm^{-1} from the bending of H–O–H bond had an additional shoulder at ~ 1580 cm^{-1} . This was a frequency characteristic of aromatic skeletal vibrations. The spent catalyst also showed a band at 1485 cm^{-1} and 1445 cm^{-1} . According to Ryczkowski [28] those bands could be related to the aromatic C–C stretching.

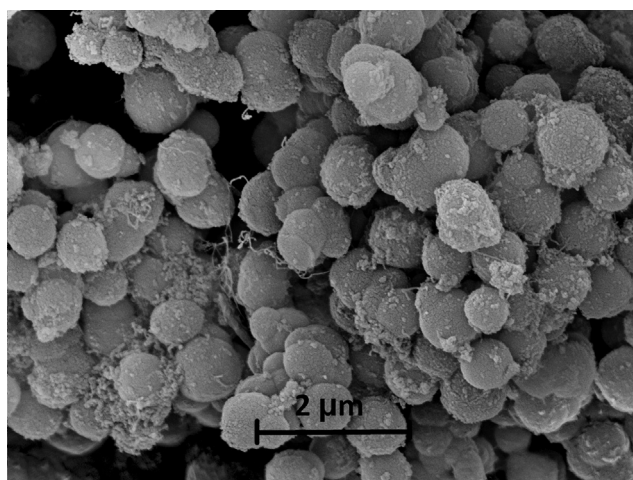


Fig. 4 – SEM micrographs of the 11%Ni@SiO₂ catalyst after 4 h reaction at 550 °C. The feedstock composition CH₄:CO₂:H₂O:O₂:He was respectively 1:0.5:0.5:0.1:0.4, CH₄ 25 ml min^{−1} over 0.2 g of the catalyst.

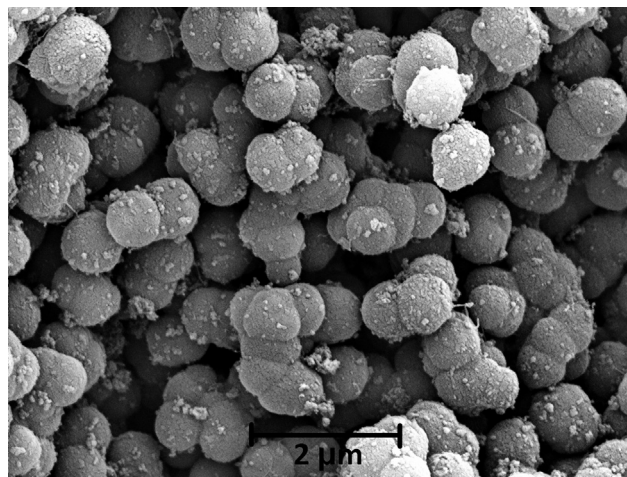


Fig. 5 – SEM micrographs of the 11%Ni@SiO₂ catalyst after 4 h reaction at 750 °C. The feedstock composition CH₄:CO₂:H₂O:O₂:He was respectively 1:0.5:0.5:0.1:0.4, CH₄ 25 ml min^{−1} over 0.2 g of the catalyst.

Conventional coke usually has an aromatic character. The IR results obtained confirmed the presence of coke. However, from IR results of analysed samples it was difficult to determine unquestionably the form of deposited coke. Because of the small amount of deposited coke, all samples were analysed in situ without catalyst etching. As a result, intensive bands related to the catalyst surface overlapped part of the bands related to deposited coke.

No diffraction peaks were detected in the XRD patterns of the fresh or the spent catalyst. Even after reaction at high 750 °C reaction temperature the Ni@SiO₂ catalyst was still in an amorphous form. The eventual Ni crystals were highly dispersed and were below the XRD detection level.

From all the tested reaction conditions the optimal for tri-reforming over the 11%Ni@SiO₂ catalyst was determined to be the feed composition with molar ratio CH₄:CO₂:H₂O:O₂:He

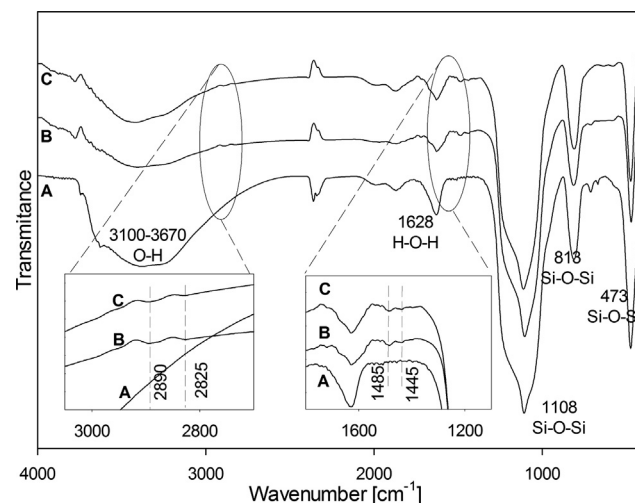


Fig. 6 – The FTIR spectra of the 11%Ni@SiO₂ catalyst: fresh (A), after 4 h reaction at 550 °C (B) and 750 °C (C). The feed composition CH₄:CO₂:H₂O:O₂:He was respectively 1:0.5:0.5:0.1:0.4, CH₄ 25 ml min^{−1} over 1 g of the catalyst.

1:0.5:0.5:0.1:0.4 at $T = 750\text{ }^{\circ}\text{C}$. For that reaction condition the H_2 :CO molar ratio was 2.5, being at the edge of acceptance for methanol synthesis. Methane conversion was high (73%) and coke deposition was very low ($5\text{ mg g}_{\text{cat}}^{-1}$).

Commercial catalyst HiFUEL™ R110 from Alfa Aesar with higher nickel loading 14.5% showed slightly lower CH_4 conversion (71%) and slightly higher CO_2 conversion (65%) at the same reaction condition. The molar ratio of H_2 :CO in syngas was lower 2.1 but coke deposition was much higher $126\text{ mg g}_{\text{cat}}^{-1}$.

Conclusion

The tested catalyst showed stable activity during the first 4 h of tri-reforming at $750\text{ }^{\circ}\text{C}$. In the tri-reforming process over the 11%Ni/SiO₂ catalyst above 70% methane conversion was obtained in the tested temperature range $550\text{--}750\text{ }^{\circ}\text{C}$. The H_2 :CO molar ratio of ~ 2.5 was obtained from the reaction at $750\text{ }^{\circ}\text{C}$. Syngas with different H_2 :CO molar ratios was obtained by varying the feedstock gas composition. For the tested catalyst, increasing the amount of oxygen in the feedstock improved methane conversion to 90% and reduced coke deposition but did not improve the H_2 :CO ratio in produced syngas. Reduction of steam partial pressure to zero reduced the H_2 :CO molar ratio in produced syngas to value ~ 2 and increased CO_2 conversion to over 90%. However, methane conversion decreased over the same range of compositions. Increasing the amount of added steam above the molar ratio CH_4 : H_2O 1:0.5 reduced the proportion between H_2 :CO in produced syngas to ~ 1.5 without affecting methane conversion. However, coke deposition increased when more water was added to the tri-reforming process. The surface area of the catalyst decreased after tri-reforming, probably due to the Ni sintering and formation of the clusters made of 2–3 catalyst particles. The Ni/SiO₂ catalyst showed slightly higher CH_4 conversion, lower coke deposition and lower CO_2 conversion compared to the commercial catalyst HiFUEL™ R110 at the optimal for the Ni/SiO₂ catalyst conditions. The results obtained showed that the Ni/SiO₂ catalyst can be considered as a promising catalyst for the tri-reforming process.

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